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Chemical Composition of Essential Oils of *Achillea teretifolia* Willd. and *A. millefolium* L. subsp. *millefolium* Growing in Turkey

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The chemical composition of the essential oils of dried aerial parts of *Achillea teretifolia* and *A. millefolium* subsp. *millefolium* were analyzed by GC and GC-MS. Sixty seven and 57 components were identified representing 95.58 and 91.41 % of the oils, respectively. 3-Cyclohexen-1-one (21.61 %), linalool (14.32 %), 1,8-cineole (12.71 %), chrysanthenone (8.55 %), *trans*-chrysanthenol (7.83 %) and δ-cadinene (4.04 %) were found to be the major components in *A. teretifolia* while δ-cadinene (19.03 %), limonene oxide (10.13 %), alloaromadendrene (6.37 %), caryophyllene oxide (5.71 %) and *trans*-caryophyllene (4.89 %) were found as major constituents in *A. millefolium* subsp. *millefolium*.

Key Words: *Achillea teretifolia*, *Achillea millefolium* subsp. *millefolium*, Asteraceae, Essential oil composition, GC-MS.

INTRODUCTION

The genus *Achillea* belongs to the Compositae family, which is one of the largest families of flowering plants. The genus *Achillea* (Asteraceae) is represented by 42 species, 20 being endemic in Turkey[1,2]. *Achillea teretifolia* Willd., an endemic plant of the flora of Turkey and *A. millefolium* L. subsp. *millefolium* (yarrow) Milfoil are perennial plants with medicinal value. The species of *Achillea* genus are known in Anatolia as "civan percemi", "pire otu" and yilan cicegi". Some *Achillea* species have ethnopharmacologic importance as known to be used in folk remedies for various purposes[3].

Some researches confirmed the presence of new chemotypes based on major chemical components of essential oil from yarrow samples collected from different parts of their country[4,5]. Mockute and Judzentiene[4] reported the essential oil composition of four chemotypes of *A. millefolium* in Lithuania. In Iran, most of the research in *Achillea* were conducted using one species originated from a limited geographical area[6-9] and some studies were focused on aerial parts mainly flowers using a limited accession from a few species[10-12]. However, there are no comprehensive researches in assessment of essential oil of *A. teretifolia* and *A. millefolium.*

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Achillea species have been used since long time for their medicinal, agricultural, cosmetic and fragrance properties. In particular, the well-known *A. millefolium* has been used as medicine by many cultures for hundreds years and is now listed in several pharmacopoeias[13,14]. As part of research on the *Achillea* genus[15-18], in the present work we report the chemical composition of the oil obtained by hydrodistillation from the aerial parts of *A. teretifolia* and *A. millefolium* subsp. *Millefolium* and analyzed by gas chromatography to mass spectrometry (GC-MS).

EXPERIMENTAL

Plant source: *Achillea teretifolia* specimens were collected from natural habitats in Elazig and *A. millefolium* subsp. *millefolium* specimens were collected in Elazig, in 2008 Kocak-1146 and1047. Voucher specimens are kept at the Firat University Herbarium (FUH).

Isolation of the essential oils: Air-dried aerial parts of the plant materials (100 g) were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h to yield.

Gas chromatographic (GC) analysis: The essential oil was analyzed using HP 6890 GC equipped with and FID detector and an HP-5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 μm) capillary column was used. The column and analysis conditions were the same as in GC-MS. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

Gas chromatography/mass spectrometry (GC-MS) analysis: The oils were analyzed by GC-MS, using a Hewlett Packard system. HP-Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Res. Lab. (BUBAL) in Firat University. HP-5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 μm) was used with helium as the carrier gas. Injector temperature was 250 ºC, split flow was 1 mL/min. The GC oven temperature was kept at 70 ºC for 2 min and programmed to 150 ºC at a rate of 10 ºC/min and then kept constant at 150 ºC for 15 min to 240 ºC at a rate of 5 ºC/min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries (WILEY, NIST). The identified constituents of the essential oils are listed in Table-1.

RESULTS AND DISCUSSION

The essential oil yields of *A. teretifolia* and *A. millefolium* subsp. *millefolium* were 0.6 and 0.8 % v/w, respectively. The result of the analysis of *A. teretifolia* and *A. millefolium* subsp. *millefolium* essential oils are present in Table-1. In case of *A. teretifolia*, 67 compounds were identified representing 95.58 % of the oils. 3-Cyclohexen-1-one was determined to be present at the high percentage (21.61 %). The presence of linalool (14.32 %), 1,8-cineole (12.71 %), chrysanthenone (8.55 %)

TABLE-1
CONSTITUENTS OF THE ESSENTIAL OILS FROM *Achillea teretifolia* AND *A. millefolium*

No	Compounds	RRI	*A. teretifolia*	*A. millefolium*
1	Santolina triene	997	0.01	–
2	α-Thujene	1016	0.02	0.02
3	α-Pinene	1021	0.22	0.78
4	Camphene	1034	0.03	–
5	Verbene	1037	–	0.03
6	Benzaldehyde	1043	0.03	–
7	Sabinene	1052	0.93	2.72
8	β-Pinene	1056	0.46	0.34
9	β-Myrcene	1063	0.30	–
10	1-Phellandrene	1077	0.10	–
11	α-Terpinene	1085	0.10	0.09
12	Benzene,1-methyl-4	1091	0.37	2.27
13	1,8-Cineole	1198	11.72	2.27
14	Benzeneacetaldehyde	1106	–	0.03
15	1,3,6-Octatriene	1107	–	0.03
16	γ-Terpinene	1117	0.27	0.22
17	*trans*-Sabinene hydrate	1126	2.07	0.30
18	α-Terpinolene	1137	0.06	–
19	Fencholenic aldehyde	1140	0.08	–
20	*cis*-Sabinene hydrate	1149	–	0.29
21	Linalool L	1152	14.32	–
22	Chrysanthenone	1167	8.55	–
23	1,7-Octadien-3-one	1175	0.15	–
24	*cis*-Verbenol	1179	1.52	1.95
25	Limonene oxide	1182	–	10.13
26	*trans*-Chyranthenol	1195	7.83	–
27	Borneol L	1201	0.26	–
28	3-Cyclohexen-1-ol	1205	1.30	0.90
29	α-Terpineol	1216	3.82	2.28
30	2-Cyclohexen-1-ol	1225	0.47	–
31	6-Octen-1-ol	1231	0.64	–
32	3,6-Octadien-1-ol	1241	0.21	–
33	*E*-Ocimenon	1245	0.13	–
34	2,3-Epoxycarene	1259	–	2.69
35	3-Cyclohexen-1-one	1264	21.61	–
36	4-Thujene-2-α-ylacetate	1269	–	0.24
37	Lavandulyl acetate	1280	0.18	2.27
38	Benzene methanol	1289	0.03	–
39	Cyclohexansiloxane	1297	0.11	–
40	Myrtenyl acetate	1316	0.02	0.08
41	Geranyl acetate	1338	0.16	–
42	Phenol,2-methoxy-4	1340	0.25	0.09
43	Neryl acetate	1345	0.23	2.51
44	α-Copaene	1360	–	0.05
45	β-Ourbonene	1366	–	0.06
46	*cis*-Jasmone	1372	–	0.10
47	3,5-Heptadienal	1374	1.97	–
48	*trans*-Caryophyllene	1393	1.02	4.89
49	*trans*-β-Farnesene	1407	–	0.05
50	α-Humulene (α-caryophyllene)	1418	0.18	0.44
51	α-Gurjunene	1419	–	0.48

52	Neoalloocimene	1421	0.24	–
53	Cycloheptasiloxane	1425	0.14	–
54	Naphthalene (β-selinene)	1430	0.18	–
55	Germacrene D	1435	0.33	2.41
56	Bicyclogermacrene	1445	0.16	0.47
57	β-Bisabolene	1452	–	0.11
58	Naphthalene (α-amorphene)	1456	0.41	–
59	δ-Cadinene	1459	–	0.24
60	Cyclohexanol	1460	–	0.24
61	Germacrene B	1470	0.06	0.21
62	Elemol	1478	0.13	0.61
63	Nerolidol	1485	0.63	2.86
64	(+) Spathulenol	1495	0.59	–
65	Caryophyllene oxide	1498	1.33	5.71
66	γ-Himachelene	1506	–	0.67
67	α-Guaiene(Ledol)	1511	0.23	0.75
68	Phenol	1514	0.40	–
69	β-Thujaplicin	1515	–	3.12
70	Epiglobulol	1521	–	0.55
71	γ-Gurjunene	1523	–	0.80
72	Alloaromadendrene	1526	–	6.37
73	δ-Cadinene	1529	4.04	19.03
74	α-Cadinol	1532	1.51	–
75	β-Eudesmol (t-muurulol)	1540	1.11	3.50
76	Azulene	1542	–	3.34
77	Caryophyllenol II	1547	0.21	0.89
78	α-Farnesene	1553	0.30	–
79	*trans*-Caryophyllene	1566	0.15	–
80	E-citral	1569	0.35	–
81	Azulen	1578	0.10	–
82	*trans*-Carveole	1606	–	0.46
83	2-Pentadecanone	1631	–	0.05
84	15-Hexadecanolide	1634	0.13	–
85	(-) Dehydroaromadendrene	1678	–	0.02
86	Hexadecanoic acid	1692	–	0.04
87	1-Heptadecanol	1706	–	0.02
88	1-Octadecanol	1778	0.01	0.05
89	Cyclononasiloxane	1853	0.04	–
90	β-Humulene	1856	–	0.06
91	Ethanol	1863	0.01	–
92	1-Eicosanol	1896	0.01	–
93	Tricosane	1903	0.03	0.13
94	Docosane	1941	0.03	–

and *trans*-chrysanthenol (7.83 %) were also important for the oil profile (Table-1). A comparison of the data presented in present studies with those in the literature for other species of *Achillea* show that there are qualitative and quantitative differences in the levels of some of the compounds present. The oil obtained from the aerial parts of *A. teretifolia* is reported to contain a high percentage of eucalyptol (1,8-cineole) (19.9 %)[19].

Other species of the genus *Achillea*, rich in linalool; *A. millefolium*[20], *A. nobilis* subsp. *sipylea* and *A. nobilis* subsp. *neilreichii*[21]. Considerable amounts of 1,8-cineole include; *A. schischkinii*[20], *A. nobilis* subsp. *sipylea* and *A. nobilis* subsp. *neilreichii*[21], *A. steaca* and *A. teretifolia*[19], *A. gypsicola* and *A. biebersteinii*[22], *A. umbellata*[23], *A. tenuifolia* and *A. biebersteinii*[24] and, *A. biserrata* and *A. salcifolia* subsp. *salcifolia*[25].

In case of *A. millefolium* subsp. *millefolium*, 57 components were identified representing 91.41 % of the oil (Table-1). δ-Cadinene was the predominant compound (19.03 %) followed by limonene oxide (10.13 %), alloaromadendrene (6.37 %), caryophyllene oxide (5.71 %) and *trans*-caryophyllene (4.89 %). Caryophyllene oxide also characterizes the essential oil of *A. millefolium*[20,24].

Previous researches showed that essential oils isolated from some *Achillea* species growing in different regions of the world were characterized by the high content of oxygenated monoterpenes, 1,8-cineole, borneol, camphor and piperitone[19,20,26-30]. Analogously, Turkish *A. gypsicola* and *A. biebersteinii* essential oils contain mainly camphor (40.17-23.56 %), 1,8-cineole (22.01-38.09 %), piperitone (11.29-0.37 %), borneol (9.50-5.88 %), α-terpineol (1.56-5.15 %), sabinaketone (1.59-1.47 %) and terpinen-4-ol (1.39-3.26). On the other hand, the existence of these monoterpenes in the essential oils of different *Achillea* species did not seem to characterize the species *Achillea* genus, belonging to different chemotypes. For instance, it has been documented that some *Achillea* essential oils contained relatively low amounts of camphor and 1,8-cineole[26,31].

Recent researches showed that oxygenated monoterpenes and the essential oils, which are relatively rich in oxygenated monoterpenes, posses strong inhibitory effects on weed germination in comparison to monoterpenes hydrocarbons and the essential oils which are relatively rich monoterpene hydrocarbons and/or sesquiterpenes[32-39].

In conclusion, this study demonstrates the occurrence of 3-cyclohexen-1-ol/linalool L chemotype of *A. teretifolia* and δ-cadinene/limonene oxide chemotype of *A. millefolium* subsp. *millefolium* in eastern Anatolia region of Turkey. However, the absence of 3-cyclohexen-1-ol from *A. millefolium* subsp. *millefolium* chemotype studied is noteworthy.

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